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THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:

Karin Schlicht et al.

Serial No.:

10/665,412

For:

METHOD FOR THE REMOVAL OF AN IMAGING LAYER

FROM A SEMICONDUCTOR SUBSTRATE STACK

Filed:

September 18, 2003

Examiner:

Kripa Sagar

Art Unit:

1756

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27,623

Attorney Docket No.: 335.7697USU

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.131(b)

Dear Sir:

Karin Schlicht, and Mario Reybrouck applicants in the above-identified patent application, declare as follows:

1. That sometime prior to April 6, 2002, we conceived a rework process for removing an imaging layer from a substrate stack comprising a substrate, an underlayer adjacent to the substrate, and an imaging layer comprising silicon placed adjacent to the underlayer.

The above process involves the steps of: (a) contacting the substrate stack with an imaging layer removal solvent; (b) removing the imaging layer with an imaging layer removal solvent thereby forming a substrate/underlayer stack, wherein said imaging layer removal solvent is selected from glycol ethers, ketones, esters, lactates, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahyd ropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and any combinations thereof; and (c) removing the imaging layer removal solvent from the substrate/underlayer stack after the imaging layer is removed.

2. We also conceived a lithographic imaging rework process for correcting one or more defects on an imaging layer on a substrate stack. The substrate stack comprises a substrate, an underlayer adjacent to a substrate, and an imaging layer comprising of silicon adjacent to the underlayer.

The above process comprises the steps of: (a) contacting the substrate stack with an imaging layer removal solvent selected from glycol ethers, ketones, esters, lactates, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahydropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and any combinations thereof; (b) removing the imaging layer with the imaging layer removal solvent, thereby forming a substrate/underlayer stack; (c) removing the imaging layer removed; (d) coating the substrate/underlayer stack after said imaging layer is removed; (d) coating the substrate/underlayer stack with a new imaging layer; (e) exposing the new imaging layer to radiation; and (f) developing the new imaging layer.

3. In addition, we concieved a rework process for removing an imaging layer from a substrate stack, said stack comprising a substrate, an underlayer adjacent to said substrate, and an imaging layer comprising silicon adjacent to said underlayer.

The process comprises the steps of (a) contacting the substrate stack with an imaging layer removal solvent; (b) removing said imaging layer with the imaging layer removal solvent thereby forming a substrate/underlayer stack, wherein the imaging layer removal solvent is selected from the group of glycol ethers, ketones, esters, lactates, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahydropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and

any combinations thereof; (c) rinsing said imaging layer removal solvent from the substrate/underlayer stack with a rinse solution after the imaging layer is removed; and (d) baking the substrate/underlayer stack to remove said rinse solution.

- 4. Attached hereto is Exhibit A which is a Company Internal Report written by Karin Schlicht sometime prior to April 6, 2002 setting forth evidence of the above rework process using propylene glycol monomethyl ether acetate (PGMEA) as a solvent, for example, indicated by "RER 600." The report demostrates inventor's possesion of the inventive concept of using the PGMEA solvent system in combination with a substrate for stipping the imaging layer without a bake step as declared under section (1) above.
- 5. Attached hereto is Exhibit B which is a Company Internal Report written by Karin Schlicht sometime prior to April 6, 2002 setting forth evidence of the above rework process using a propylene glycol monomethyl ether acetate (PGMEA)/EL mixture, and PGME as solvents. The report demostrates the inventor's possesion of the inventive concept of using a PGMEA solvent system in combination with a substrate for stipping the imaging layer with a bake step as declared under section (2) above.
- 6. Attached hereto is Exhibit C which is a Company Document created and presented by Karin Schlicht prior to April 6, 2002 setting forth evidence of the above rework process, as a whole, using propylene glycol monomethyl ether acetate PGMEA/EL mixtures and PGMEA/PGME/MPK compositions as a solvents. The report demostrates the inventor's possesion of the inventive concept of using a PGMEA solvent system in combination with a substrate for stipping the imaging layer with relevant bake steps as declared under section (1-3) above.
- 7. We further declare that all statements made herein of our knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Declared at <u>F. Pr</u>	Ouidana, U.S.A. this 13	Lday of Dec	Des
Dara:	Scale Karin Schlic	ht,	
Declared at	, Belgium this	day of	, 2004.
	Mario Revhr	rouck	

Declared at	, U.S.A. this	day of	, 2004.
	Karen Sc	chlicht,	
Declared at	Belgium this	5 <u>/ 0</u> day of <u></u>	ecember, 2004.
la	Mario Re	eybrouck.	
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EXHIBIT A



Formulated Products

ARCH Chemicals, Inc.

East Providence, RI

Report Title:

248 TIS Imaging Layer Rework

Requested

Internal

By:

Subject:

Screening materials to rework 248 TIS Imaging Layer

Conclusions:

A rework process with RER 600 worked on the FTCU, but needs further

optimization for the new underlayer. RER 651 and a PGMEA/EL mixture

resulted in clean imaging after 1x rework.

Keywords:

TIS 248, TIS 193, Rework, RER 600, RER 651, Imaging Layer

Report Written by:

Karin Schlicht

Work Performed by:

Jeff Eisele, Pat Morra, Ken Uhnak, Karin Schlicht

Classification:

Restricted to ARCH.

Introduction:

Work has been done my Mario Reybrouck at IMEC on the 248 nm TIS system. The following results were obtained:

RER600 was successfully used on the FFA UL. This was a 5-60 min. immersion process, followed by a water rinse, and a 90" proximity bake @ 100 C. The 100 C temperature was chosen to drive off excess water. After re-imaging a new IL the process window was virtually identical. FTIR results also showed that the UL was unchanged after the rework process.

Objective:

Re-create IMEC results at QP and find new solvent system that can be marketed for TIS rework.

Experimental:

The following factors will be studied:

- 1. "old" FFA vs new imaging system
- 2. Bake step after stripping of the UL
- 3. Water rinse (Cascade rinse followed by spin rinse dryer)

The following experimental matrix will investigate these variables as well as look into new solvents mixtures:

Imaging System	Bake Temp	Stripper
Old IL/UL	100 C	RER600
new IL/UL	100 C	RER600
new IL/UL	205 C	RER600
new IL/UL	100 C	RER651
new IL/UL	100 C	PGMEA/EL
new IL/UL	100 C	PGMEA/MPK
new IL/UL	on track/no water rinse	RER600

Two wafers were processed for each condition. Most wafers were stripped in a bath with agitation at room temperature. A DNS coating track was used to strip wafers for the track process. Here RER 600 was applied dynamically to strip off the imaging layer. These wafers were subsequently spun dry, but no additional bake step was used.

Best energy and focus were found for the control wafers (no rework). SEM pictures for the reworked wafers were then taken at the same energy and focus settings.

Results:

SEM micrographs are attached to the PDF version of this report. Results from the duplicate wafers show that there is noise in the stripping process.

RER 600 was used to investigate the influence of the dehydration bake and a track process without water rinse or dehydration bake.

The track process resulted in clean profiles without footing on one of the wafers, but had scumming on another. This shows that the process works but needs optimization. (RER 600 was hand dispensed). Wafers with a 205 C dehydration bake had no scumming between the lines, but some footing is visible. At the 100 C bake images showed bad footing.

Work done on the FTCU ("old") with RER 600 showed comparable results to the control.

RER 651 and a mixture of PGMEA and EL resulted in clean imaging after rework, while a mixture of PGMEA and MPK showed severe scumming. I did not expect this degee of scumming since RER 651 also contains MPK.

Conclusions:

A rework process with RER 600 worked on the FTCU, but needs further optimization for the new underlayer. RER 651 and a PGMEA/EL mixture resulted in clean imaging after 1x rework.

Future Work:

- 1. This work needs to be repeated for the 193 IL/UL.
- 2. Repeated rework with best stripper solution.
- 3. Test UL integrity by FTIR.

EXHIBIT B



Formulated Products

ARCH Chemicals, Inc.

East Providence, RI

Report Title:

193 IL Removal – Part 1

Requested By:

Internal

Subject:

Test IL removal chemistries with TIS 193 nm system. Chemistries chosen were

successful with the TIS 248 nm system.

Conclusions:

PGMEA as the solvent to remove the imaging layer appears to cause adhesion

failure after subsequent processing. However, when PGMEA is mixed with EL or

PGME scumming can occur. Optimization may be possible.

Keywords:

TIS 193, IL rework, TIS2200UL, TIS2000IL-05

Report Written by:

Karin Schlicht

Work Performed by:

Karin Schlicht, Pat Morra, Paul Berard

Classification:

Restricted to ARCH.

Distribution:

ARCH employees

Introduction:

The imaging layer rework with the TIS 248 nm system was successful with RER651 and a PGMEA/EL mixture⁽¹⁾. RER 600 also showed promise. In this experiment we are examining if the same chemistries can be used for the rework of the imaging layer of the TIS 193 nm system.

Description of Procedure:

The following experimental matrix was employed:

Chemical	Strip Time [minutes]	Dehydration Bake Temperature [°C]
PGMEA	5	105
PGMEA	5	205
PGMEA	0.5	None*
PGMEA/MPK 99/1	5	105
PGMEA/EL 90/10	5	105
RER 651	5	105
RER 651	10	105
RER 651	20	105

^{*} Track process

Wafers were processed as follows:

- 1. Wafers processed through development according to the lithographic process listed below in an amine controlled clean room environment.
- 2. All, but one of the wafers had the IL stripped according to the experimental plan in a non-amine controlled clean room chase area. Stripping was done in a batch mode by immersion. This was followed by a cascade water rings and spin rinse drying. One wafer was stripped on the SVG coat module applying the strip solution on a wafer while spinning @ 500 rpm.
- 3. Re-imaging according to the lithographic process. Control wafers were imaged only once.
- 4. SEM micrographs were taken at best energy and focus found for the control wafers (profile and CD measurements only)

Materials and Lithographic Process Parameters:

Parameter	Value
TIS 2200UL lot	K007583
TIS 2200UL process	Parameter
	Value
	Coating Equipment
	Optitrak
	Film Thickness
	5000 Å
	Film Cure
	70" @ 205 °C
TIS2000IL-5 Lot	K007544
TIS2000IL-5 process	Parameter
	Value
	Coating Tool
	SVG
	Film Thickness
	2350 Å
	Soft bake
	60" @ 135 ℃
	Exposue tool
	193 Microstep
	Exposure Energy
	18 mJ/cm ²
	Develop Tool
	SVG
	PEB
	60" @ 125 ℃
	Developer
	OPD 262

Develop process 7"/58" stream/puddle
SEM Tool Hitachi 4100 or 4200

Results:

The immersion process with PGMEA resulted in adhesion loss with both the 105 °C and 205 °C dehydration bakes. The formulation with 1 % MPK added the PGMEA had resulted in the same failure. All other conditions, including the PGMEA strip on the SVG track, resulted in severe scumming. (See attached SEM micrographs)

At this point it is not clear if the solvent treatment or any of the other processing steps is the cause for the lifting or the scumming. The processing will be studied in a separate experiment.

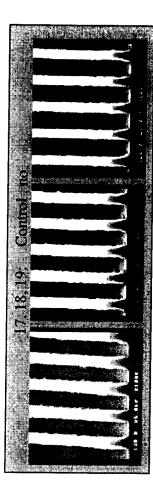
Conclusions:

PGMEA as the solvent to remove the imaging layer appears to cause adhesion failure after subsequent processing. However, when PGMEA is mixed with EL or PGME scumming can occur. Optimization may be possible.

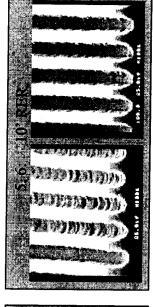
Reference:

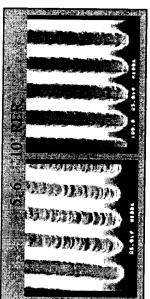
- (1) Internal report issued by Author "248 TIS Imaging Layer Rework", Nov. 29th 2001
- (2) Work Request 1212-3290

TIS2000IL-5 Rework (193nm) 130 nm images after 1 x rework











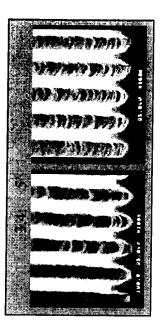


EXHIBIT C

TIS 2000 Rework/Cleaning

Karin Schlicht

248/193 TIS Cleaning Projects

248 SYSTEM

193 SYSTEM

- Imaging Layer removal
- UL removal
- Clean after UL etch
- Clean after pattern transfer
- Imaging Layer removal
- UL removal
- Clean after UL etch
- Clean after pattern transfer

248 IL LSM-96-006 Removal

Work done at QP and IMEC

Materials and Lithographic Process Parameters (QP) LSM-96-006 Rework (248nm)

UL Process

IL Process

lot K007528

Material

90" @ 135 °C 2350 Å	Canon EX6	NA/o 0.65/0.8/0.5	to match control	90" @ 125 °C	OPD 262
Soft Bake Film Thickness	Exposure tool		Exposure E/F	PEP	Developer
lot K007553	5000 Å	10000			
Material Cure process	Film Thickness				

Hitachi 4100/4200

by cross-section

7,,/28,,

stream/puddle

SEM analysis

Develop process

LSM-96-006 Rework (248nm) Base Rework Process Flow (QP)

- Coat UL
- Image 1st layer
- Coat IL
- Expose IL
- Develop IL
- Strip IL
- Immerse in solvent
- Cascade water rinse
- Spin Rinse dryer
- Dehydration Bake (DHB)

- Image 2nd layer
- Coat IL
- Expose IL
- Develop IL
- SEM Analysis
- Get best Energy and Focus from controls
- Take SEM from samples @
 best E/F from control
 wafers

UL Film Thickness Retention after Stripping LSM-96-006 Rework (248nm)

248nm

TIS248UL-01-50, lot= K007590 TSI248IL-01-23, lot= K007570-F04

Fth-measurements

after 5min RER 600

							-
Wafer	before	Filmthickness	st-dev	3 sigma	min	max	range
900	550.84nm	550.45	1.454	4.362	547.84	554.63	6.79

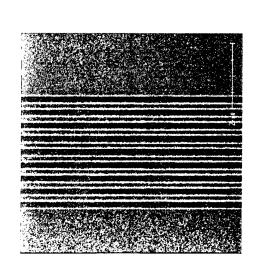
after 5min RER 651

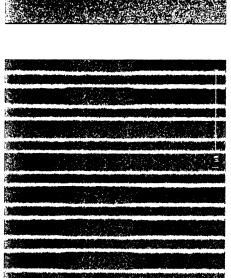
Wafer	pefore	Filmthickness	st-dev	3 sigma	min	max	range
D08	551.44nm	551.77	1.648	4.944	549.03	554.23	5.2

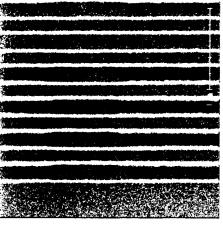
^{*} Wafers after a few seconds clean (visual inspection)

248nm TIS Rework

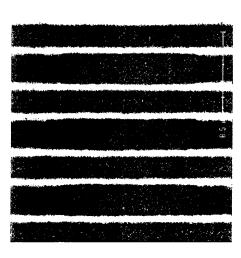
T010844 D14 RER600

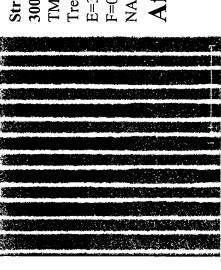






T010844 D15 RER651



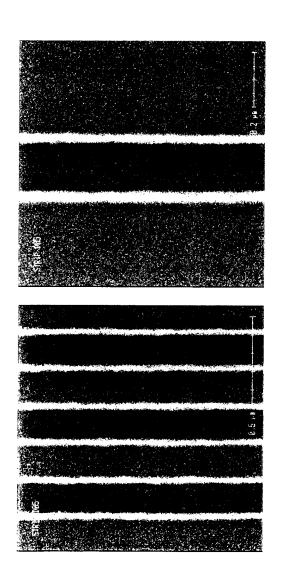


Strip248nm

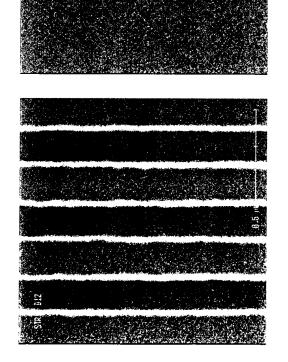
300nm IL K007570-F04 -550nm K007590 TM99DF_TDF_V01 Trench 200nm E=30 mj/cm2/2 F=0.1/0.1 NA 0.63 Sigma 0.5

After 2X rework

T010844 D15 RER651



T010844 D14 RER600



Strip 248nm

300nm IL K007570-F04 - 550nm K007590 TM99DF_TDF_V01 Trench 200nm E=30 mJ/cm²/2 F=0.1/0.1μm NA 0.63 Sigma 0.5

After 3X rework

LSM-96-006 Rework (248nm) 200 nm images after 1 x rework Process Window for RER600 and RER651

RER 600

	Exp	Expose Latitude [%]	de [%]		DOF [um	[m]
Rework	Dense	Iso	Focus [um]	Dense	Iso	Energy [mJ/cm2]
none	20.2	24.6	0.1	0.7	9.0	36
1 X	19.9	25.2	0.1	0.55	9.0	34
2 X	17.6	23.3	0.1	0.55	0.5	34
3 X	18.1	25.3	0.1	0.55	0.5	34

R 651

	Exp	Expose Latitude [%]	de [%]		DOF [um]	m
Rework	Dense	Iso	Focus [um] Dense	Dense	Iso	Energy [mJ/cm2]
none	20.2	24.6	0.1	0.7	9.0	36
1 X	23.7	25.2	0.1	0.7-0.8	9.0	36-38
2 X	18.7	23.1	0.1	0.4	0.5	34
3 X	22.3	32.2	0.1	0.7	0.5	36

Data generated by Mario Reybrouck at IMEC

193 IL TIS2000 IL-5 Removal

Work done at QP and IMEC

Materials and Lithographic Process Parameters (QP) TIS2000IL-5 Rework (193nm)

UL Process

IL Process

Material Material	Lot K007583	Material	
Cire process	70, 30 30 ° 30 ° 30 ° 30 ° 30 ° 30 ° 30 °	Soft Bake	
care process	70 (66 202)	Eilm Thiolmon	`
Film Thickness	5000 Å		•

Soft Bake 60" @ 135 °C Film Thickness 2350 Å Exposure tool 193 ISI Microstep Exposure E/F to match control PEP 60" @ 125 °C Developer OPD 262 Develop process 7"/58" stream/puddle
SEM analysis by cross-section

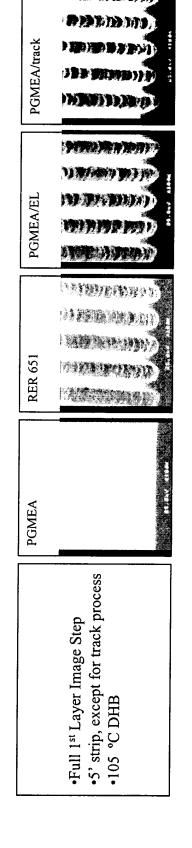
Hitachi 4100/4200

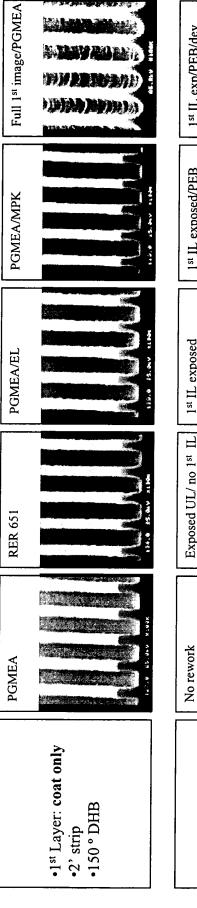
TIS2000IL-5 Rework (193nm) Base Rework Process Flow (QP)

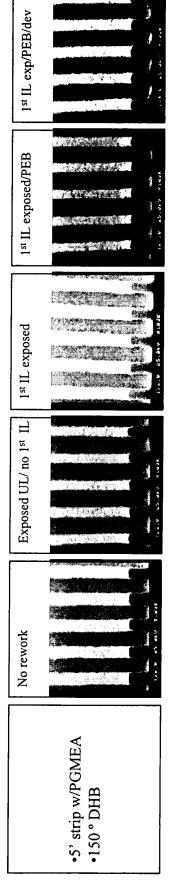
- Coat UL
- Image 1st layer
- Coat IL
- Expose IL
- Develop IL
- Strip IL
- Immerse in solvent
- Cascade water rinse
- Spin Rinse dryer
- Dehydration Bake (DHB)

- Image 2nd layer
- Coat IL
- Expose IL
- Develop IL
- SEM Analysis
- Get best Energy and Focus from controls
- Take SEM from samples @
 best E/F from control
 wafers

TIS2000IL-5 Rework (193nm) 130 nm images after 1 x rework Summary







TIS2000IL-5 Rework (193nm) Processing Conditions Studied with Good Results Summary

Process Conditon	Ranges	Comments
DНВ	105-205 C	UL only; @ 205 C about 30 A Film Thickness Loss
UL left in chase near strip station	up to 48 hours	UL only
DI water rinse	Cascade/spin rinse dry	UL only
Developer	with and w/o PEB	UL only
HF dip	up to 5 minutes	UL only
UL cure time	60-120 seconds	1st IL coat only
DHB	105 - 180 C	1st IL coat only
Strip time	1-5 min	IL coat only/PGMEA strip
Imaging steps	exposure through PEB	UL only or UL/IL stack

T010385 D17 RER600 T001153 D10 RER651 193nm TIS (2*bake steps before exposure) 193nm TIS Rework NA 0.63 Sigma 0.5 after 1X rework 265nm IL K007547 - 550nm K007563T TM99DF_TDF_V01 Trench 150nm E=9 mJ/cm2/0.1 F=0.1/0.1E=9.4 mj/cm2 Two bake steps before exposure after rework: * 105°C/90" * 205°C/90"

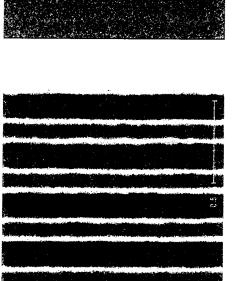
Strip 193nm

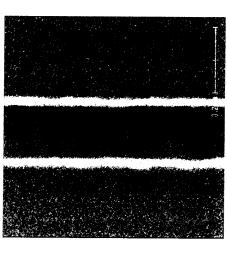
265nm IL K007547 - 550nm K007563T TM99DF_TDF_V01 Trench 150nm E=9 mj/cm2/0.1 F=0.1/0.1 Strip 193nm

193nm TIS Rework

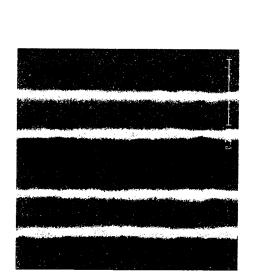
NA 0.63 Sigma 0.5 Na 2X rework

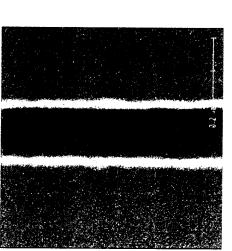
T010385 D22 RER600





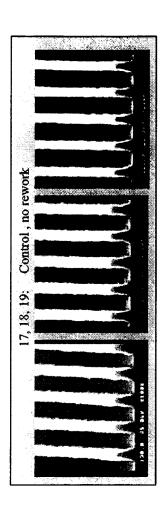
T000058 D15 RER651



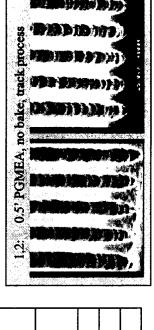


exposure after rework: * 105°C/90" One bake steps before

TIS2000IL-5 Rework (193nm) 130 nm images after 1 x rework Test Rework Chemistries



Chemical	Strip Time	Dehydration	Results
	[minutes]	Bake	
		Temperature	
		[,c]	
PGMEA	5	105	105 lifting
PGMEA	5	205	205 lifting
PGMEA	0.5*	None*	scumming
PGMEA/MPK	5	105	105 lifting
99/1			
PGMEA/EL	5	105	105 scumming
90/10			
RER 651	5	105	105 scumming
RER 651	10	105	105 scumming
RER 651	20		105 scumming
- -	. !		

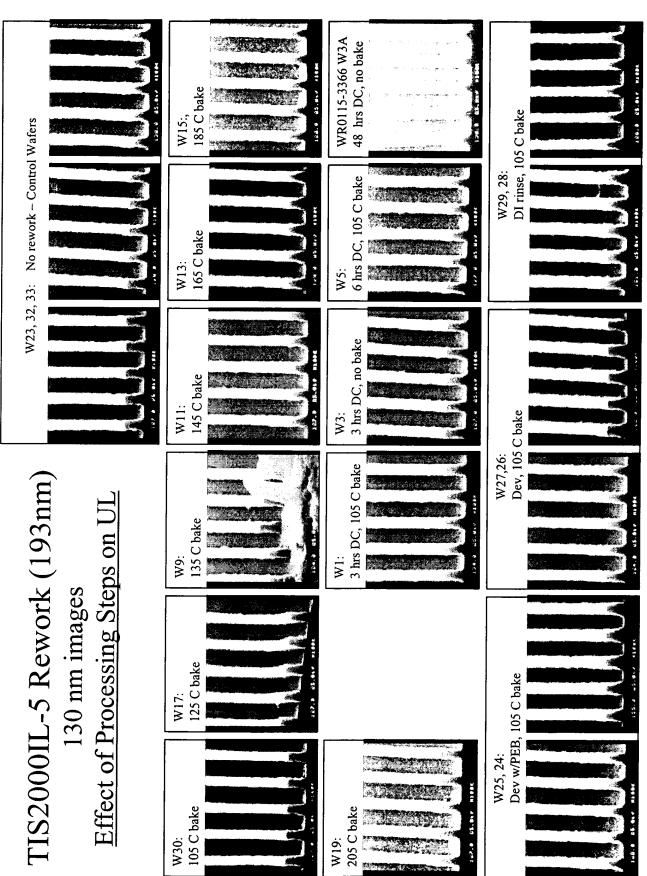


* Track strip process

TIS2000IL-5 Rework (193nm) 130 nm images after 1 x rework Effect of Processing Steps on UL

UL left in	Dehydration	Develop/rinse	Results
'Dirty	Bake		
Chase' (DC)	Temperature		
[hours]	[,c]		
3	105	none	poog
3	none	none	poog
9	105	none	poob
48	auou	none	poob
0	105	none	poob
0	125	none	poob
0	135	none	poob
0	145	none	poob
0	165	none	poob
0	185	none	poob
0	205	euou	poob
0	105	Develop w/PEB	poob
0	105	Develop w/oPEB	poob

In this experiment the 1st imaging step was skipped.



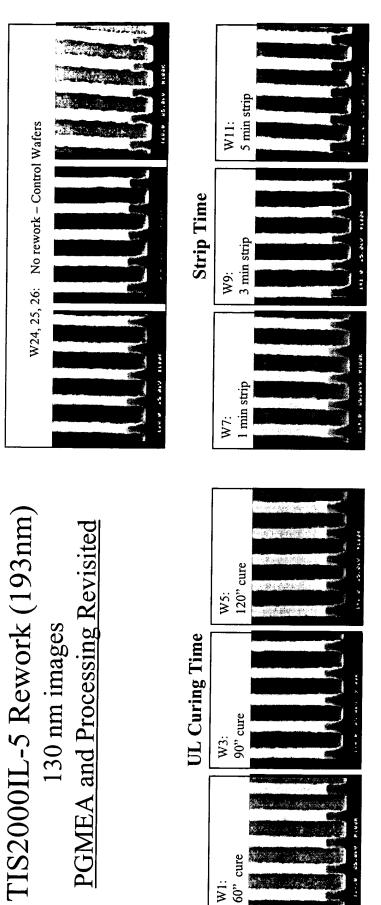
TIS2000IL-5 Rework (193nm) 130 nm images PGMEA and Processing Revisited

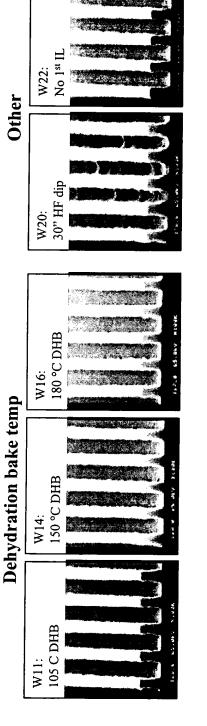
In this experiment we attempted to make PGMEA as stripping solution work by modifying base processes.

Unless otherwise noted, the 1st IL was coated only. To save time exposure and development were skipped.

130 nm images

Control



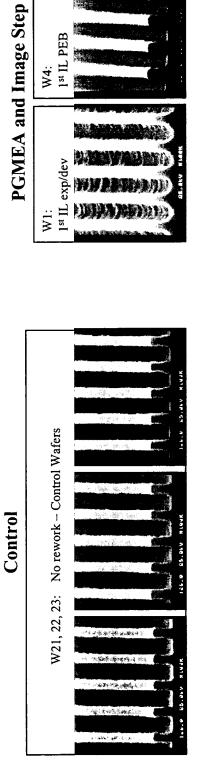


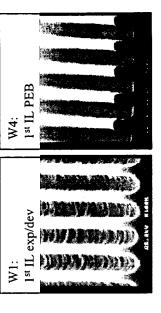
TIS2000IL-5 Rework (193nm) 130 nm images Rework Chemistries Revisited

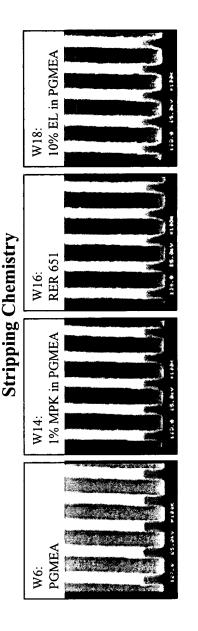
Chemical	Other	Results
	Treatment	
PGMEA	1st IL exp/dev	scnm
PGMEA	1st IL PEB	poob
PGMEA		poog
PGMEA/M		
PK 99/1		good
PGMEA/EL		
90/10		goog
RER 651		poop

Unless otherwise noted, the 1st IL was coated only. Based on earlier experiments the DHB temperature was changed to 150 C, and strip time was 2 minutes.

TIS2000IL-5 Rework (193nm) Rework Chemistries Revisited 130 nm images



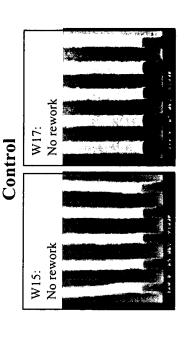




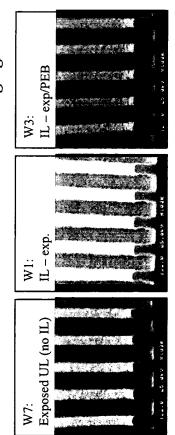
TIS2000IL-5 Rework (193nm) 130 nm images Imaging Process and HF Dipping

What in the imaging process	caused the failure after	HE din was done to see if	onid formation during impaire	acid tormation during imaging	has a negative impact on IL	rework. If 1st IL was applied	a 5' PGMEA strip, followed	by a 150 C DHB was done.
	Results	poob	poob	poob	footing	poob	poob	poob
	HF dip [minutes]	none	none	none	none	1	2	3
	Imaging Process Steps	exbose	exbose	exp/PEB	exp/PEB/dev	auou	none	none
	1st IL coat?	Z	Y	Y	Y	Z	Z	Z

TIS2000IL-5 Rework (193nm) 130 nm images Imaging Process and HF Dipping

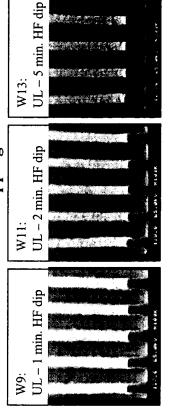


Imaging Process



W5: W6: IL – exp/PEB/dev IL – exp/PEB/dev

HF dipping



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